

Variationally corrected discrete-basis-set calculation for electron-molecule scattering in the static-exchange approximation

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We present a method for including a variational correction in the discrete-basis-set method for electron-molecule scattering introduced by Rescigno, McCurdy, and McKoy. Our prescription for variationally corrected partial-wave K -matrix elements is based on Kohn's formula for the variationally stable scattering amplitude in three dimensions. The method is applied to e^- - H_2 scattering in the static-exchange approximation, and the effect of choosing different trial basis sets is shown. Our results are in good agreement with the results of other accurate calculations.

I. INTRODUCTION

In a recent paper¹ we applied the discrete basis set method for electron-molecule scattering introduced by Rescigno, McCurdy, and McKoy²⁻⁴ to e^- - N_2 scattering in the static-exchange approximation. The method involves approximating the scattering potential by its projection onto a subspace of discrete basis functions

$$U^t = \sum_{\alpha\beta} |\alpha\rangle \langle \alpha| U |\beta\rangle \langle \beta|. \quad (1)$$

In our formulation, U^t is substituted into the Lippmann-Schwinger equation for the K matrix

$$K = U + U G_0^P K, \quad (2)$$

where G_0^P is the principal-value free-particle Green's function. This leads to a finite matrix equation:

$$\langle \alpha | K | \beta \rangle = \langle \alpha | U | \beta \rangle + \sum_{\gamma\delta} \langle \alpha | U | \gamma \rangle \langle \gamma | G_0^P | \delta \rangle \langle \delta | K | \beta \rangle. \quad (3)$$

Applications of the method to date have shown that useful scattering information can be obtained directly from the solution of Eq. (3); however, the accuracy of these results is limited by the lack of variational stability with respect to errors due to the difference $U - U^t$. In a calculation for a two-center Gaussian-model potential, Rescigno *et al.*³ obtained significantly improved results by adding an approximate variational correction. In this paper we present a method for calculating a more accurate correction for variational errors. The method is applied to e^- - H_2 scattering in the static-exchange approximation.

Our approach follows Kohn's prescription for the variationally corrected scattering amplitude in three dimensions.⁵ We obtain a variational formula of the form

$$K_{ll'm}^s = K_{ll'm}^t + \langle \psi_{out}^t | (U - U^t) | \psi_{in}^t \rangle_{ll'm}, \quad (4)$$

assuming axial symmetry for the target molecule. The trial wavefunctions ψ_{in}^t , ψ_{out}^t and the approximate K -matrix element $K_{ll'm}^t$ are constructed from the discrete basis set solution of Eq. (3). The correction term involves on- and off-shell partial-wave Born matrix elements of U , U^t , and K^t . The matrix elements of U are the same as those needed in the second Born approximation. In this work matrix elements of the static-exchange potential are calculated numerically using a single-center expansion of the target orbital. The matrix elements of U^t and K^t are calculated analytically as discussed in Ref. 1. Two advantages of our prescription are that there is no restriction on the scattering energy and the scattering boundary conditions are not approximated.

Section II contains a discussion of our variational formula and the calculation of matrix elements of U . Section III presents our results for e^- - H_2 scattering in the static-exchange approximation. Scattering in the Σ and Π symmetries is treated for incident momentum of 0.5 and 0.7 a.u. Calculations are done for several different basis sets to investigate the convergence of our corrected results with respect to changes in the trial basis set. Our corrected results for diagonal phase shifts are compared with the results of Schneider⁶ and Tully and Berry⁷ and with the results of first and second Born approximations. Atomic units are assumed throughout unless otherwise noted.

II. THEORY

In the fixed-nuclei approximation the Schrödinger equation for an elastically scattered electron is of the form

$$\left[-\frac{1}{2}\nabla^2 + V(R, \vec{r}) - \frac{1}{2}k^2 \right] \psi_k(R, \vec{r}) = 0, \quad (5)$$

where $V(R, \vec{r})$ is an optical potential for the effective interaction between the target and the scattered electron. The potential depends pa-

rametrically on the relative coordinates of the target nuclei, denoted by R . The vector subscript \vec{k} indicates the dependence of the wave function on the direction as well as the magnitude of the incident momentum for a nonspherical target. Imposing the standing-wave boundary condition leads to the asymptotic form

$$\psi_{\vec{k}}(\vec{r}) \rightarrow [e^{i\vec{k}\cdot\vec{r}} - 2\pi^2 \langle \vec{k}' | K | \vec{k} \rangle r^{-1} \cos kr] / (2\pi)^{3/2}, \quad (6)$$

as $r \rightarrow \infty$, where $\vec{k}' = k\hat{r}$ and we have chosen the normalization

$$\langle \psi_{\vec{k}} | \psi_{\vec{k}'} \rangle = \delta(\vec{k} - \vec{k}'). \quad (7)$$

The Schrödinger equation [Eq. (5)] and the standing-wave boundary condition represented by Eq. (6) correspond to the Lippmann-Schwinger equation

$$\psi_{\vec{k}} = \phi_{\vec{k}} + G_0^P(k) U \psi_{\vec{k}}, \quad (8)$$

where $U = 2V$,

$$\phi_{\vec{k}} = e^{i\vec{k}\cdot\vec{r}} / (2\pi)^{3/2} \quad (9)$$

and $G_0^P(k)$ is the principal value free-particle Green's function. In the Fourier-integral representation,

$$\langle \vec{r} | G_0^P(k) | \vec{r}' \rangle = P \int d^3k' \frac{\langle \vec{r} | \vec{k}' \rangle \langle \vec{k}' | \vec{r}' \rangle}{k^2 - k'^2}, \quad (10)$$

where $\langle \vec{r} | \vec{k} \rangle = \phi_{\vec{k}}(\vec{r})$ and P denotes principal-value integration. Using the identity

$$K \phi_{\vec{k}} = U \psi_{\vec{k}}, \quad (11)$$

Eq. (8) may be rewritten as

$$\psi_{\vec{k}} = \phi_{\vec{k}} + G_0^P(k) K \phi_{\vec{k}}. \quad (12)$$

Thus a method for calculating a basis-set representation for the K matrix leads to an approximate wave function

$$\psi_{\vec{k}}^t = \phi_{\vec{k}} + P \int d^3k' \phi_{\vec{k}'} \frac{\langle \vec{k}' | K | \vec{k} \rangle}{k^2 - k'^2} \quad (13)$$

with the asymptotic form

$$\psi_{\vec{k}}^t - \phi_{\vec{k}} - (\pi/2)^{1/2} \langle \vec{k}' | K | \vec{k} \rangle^t r^{-1} \cos kr \quad (14)$$

as $r \rightarrow \infty$. In Eq. (14)

$$\begin{aligned} \langle \vec{k}' | K | \vec{k} \rangle^t &\equiv \langle \vec{k}' | K^t | \vec{k} \rangle \\ &= \sum_{\alpha\beta} \langle \vec{k}' | \alpha \rangle \langle \alpha | K | \beta \rangle \langle \beta | \vec{k} \rangle. \end{aligned} \quad (15)$$

To obtain a formula for variationally corrected elements of the K matrix, we follow the method of Kohn for the full-scattering amplitude in three dimensions.⁵ By applying Kohn's analysis and using a standing-wave boundary condition, it can be shown that, to first order,

$$\delta \langle \psi_{\vec{k}'}^t | L | \psi_{\vec{k}}^t \rangle = -\delta \langle \vec{k}' | K | \vec{k} \rangle^t, \quad (16)$$

where

$$L = -\nabla^2 + U - k^2. \quad (17)$$

Hence, a prescription for variationally corrected K matrix elements is

$$\langle \vec{k}' | K | \vec{k} \rangle^s = \langle \vec{k}' | K | \vec{k} \rangle^t + \langle \psi_{\vec{k}'}^t | L | \psi_{\vec{k}}^t \rangle. \quad (18)$$

Since

$$(-\nabla^2 + U^t - k^2) \psi_{\vec{k}}^t = 0, \quad (19)$$

Eq. (18) can be rewritten in the distorted-wave approximation form

$$\langle \vec{k}' | K | \vec{k} \rangle^s = \langle \vec{k}' | K | \vec{k} \rangle^t + \langle \psi_{\vec{k}'}^t | (U - U^t) | \psi_{\vec{k}}^t \rangle. \quad (20)$$

To calculate the correction term in Eq. (20), we expand it using Eq. (12)

$$\begin{aligned} \langle \psi_{\vec{k}'}^t | (U - U^t) | \psi_{\vec{k}}^t \rangle &= \langle \vec{k}' | (U - U^t) | \vec{k} \rangle \\ &+ \langle \vec{k}' | (U - U^t) G_0^P K^t | \vec{k} \rangle \\ &+ \langle \vec{k}' | K^t G_0^P (U - U^t) | \vec{k} \rangle \\ &+ \langle \vec{k}' | K^t G_0^P (U - U^t) G_0^P K^t | \vec{k} \rangle. \end{aligned} \quad (21)$$

The fourth term on the right-hand side (RHS) of Eq. (21) is second order in G_0^P . For a sufficiently accurate trial basis set, we expect this term to be small compared to the others. Neglecting this term, and using the Fourier-integral representation for G_0^P we obtain

$$\begin{aligned} \langle \psi_{\vec{k}'}^t | (U - U^t) | \psi_{\vec{k}}^t \rangle &\cong \langle \vec{k}' | (U - U^t) | \vec{k} \rangle \\ &+ P \int d^3k'' \langle \vec{k}' | (U - U^t) \frac{|\vec{k}''\rangle \langle \vec{k}''|}{k^2 - k''^2} K^t | \vec{k} \rangle \\ &+ P \int d^3k'' \langle \vec{k}' | K^t \frac{|\vec{k}''\rangle \langle \vec{k}''|}{k^2 - k''^2} (U - U^t) | \vec{k} \rangle. \end{aligned} \quad (22)$$

In order to separate the dependence of the scattering on the target orientation and the scattering angle from the dynamical problem, we expand the matrix elements of K and U in a series of spherical harmonics about the center of mass in the body-fixed frame. For an axially symmetric target, these expansions have the form

$$\begin{aligned} \langle \vec{k}' | K | \vec{k} \rangle &= -\frac{1}{k} \sum_{l, l', m} i^{l-l'} \langle k' l' m | K | k l m \rangle \\ &\times Y_{l', m}(\hat{\vec{k}}') Y_{l, m}^*(\hat{\vec{k}}), \end{aligned} \quad (23)$$

and similarly for U . In Eq. (23) the ket

$$|k l m\rangle = |j_l(kr) Y_{l, m}(\hat{\vec{r}})\rangle, \quad (24)$$

where $j_l(kr)$ is a spherical Bessel function. Substituting expansion (23) for U , and similar expansions for U^t and K^t , into Eq. (22) leads to the following prescription for the variationally corrected coupled partial-wave K matrix:

$$\begin{aligned}
\langle k'l'm|K|klm\rangle^s &= \langle k'l'm|K^t|klm\rangle + \langle k'l'm|(U-U^t)|klm\rangle \\
&- \frac{1}{k} \sum_{l''} P \int dk'' k''^2 \langle k'l'm|(U-U^t) \frac{|k''l''m\rangle\langle k''l''m|}{k^2-k''^2} K^t|klm\rangle \\
&- \frac{1}{k} \sum_{l''} P \int dk'' k''^2 \langle k'l'm|K^t \frac{|k''l''m\rangle\langle k''l''m|}{k^2-k''^2} (U-U^t)|klm\rangle.
\end{aligned} \quad (25)$$

Evaluation of the terms in Eq. (25) requires partial-wave Born matrix elements of K^t , U^t , and U . The matrix elements of K^t and U^t are obtained using techniques described in Ref. 1. Matrix elements of U are calculated as discussed below. The required matrix elements of U are just those needed to evaluate the second Born approximation:

$$\langle k'l'm|K^{(2)}|klm\rangle = \langle k'l'm|U|klm\rangle - \frac{1}{k} \sum_{l''} P \int dk'' k''^2 \langle k'l'm|U \frac{|k''l''m\rangle\langle k''l''m|}{k^2-k''^2} U|klm\rangle. \quad (26)$$

For a closed-shell diatomic molecule, the static-exchange potential is of the form

$$U = -\frac{2Z}{|\tilde{\mathbf{r}} - \tilde{\mathbf{A}}|} - \frac{2Z}{|\tilde{\mathbf{r}} + \tilde{\mathbf{A}}|} + 2 \sum_{\sigma=1}^N (2J_{\sigma} - K_{\sigma}), \quad (27)$$

where the Coulomb operator

$$J_{\sigma}(\tilde{\mathbf{r}}) = \int d^3r' \frac{\phi_{\sigma}^*(r')\phi_{\sigma}(r')}{|\tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|}, \quad (28)$$

and K_{σ} is the corresponding exchange operator. The nuclear charge is denoted by Z , the nuclear centers are at $\pm\tilde{\mathbf{A}}$, and N is the number of occupied orbitals. In Eq. (28) $\phi_{\sigma}(\tilde{\mathbf{r}}')$ denotes an occupied orbital. To evaluate partial-wave Born matrix elements of the static-exchange potential

$$\begin{aligned}
\langle k'l'm|U|klm\rangle &= \langle k'l'm|U^{(s)}|klm\rangle \\
&- \langle k'l'm|U^{(ex)}|klm\rangle,
\end{aligned} \quad (29)$$

we use the single-center expansion method formulated by Faisal⁸ for the static part $U^{(s)}$, and by Burke and Sinfaillam⁹ for the exchange part $U^{(ex)}$. The method involves single-center expansions for the Coulomb interaction:

$$\frac{1}{|\tilde{\mathbf{r}} - \tilde{\mathbf{r}}'|} = \sum_{\lambda=1}^{\infty} \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} P_{\lambda}(\hat{\tilde{\mathbf{r}}} \cdot \hat{\tilde{\mathbf{r}}'}), \quad (30)$$

and the occupied orbitals

$$\phi_{\sigma}(\tilde{\mathbf{r}}) = \sum_{s=0}^{\infty} \frac{1}{r} U_s^{\sigma}(r) Y_{s m_s}(\hat{\tilde{\mathbf{r}}}), \quad (31)$$

where $P_{\lambda}(\hat{\tilde{\mathbf{r}}} \cdot \hat{\tilde{\mathbf{r}}'})$ is a Legendre polynomial. Using Eqs. (29) and (30) in the local parts of the RHS of Eq. (27) leads to a multipole expansion for the static potential

$$U^{(s)}(\tilde{\mathbf{r}}) = 2 \sum_{\lambda=0}^{\infty} V_{\lambda}(r) P_{\lambda}(\hat{\tilde{\mathbf{r}}}), \quad (32)$$

$$\begin{aligned}
V_{\lambda}(r) &= -2Z \left(\frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \right)_A + \sum_{\sigma=1}^N N_{\sigma} (-1)^{m_{\sigma}} \sum_{s,s'=m_{\sigma}}^{\infty} \frac{[(2s+1)(2s'+1)]^{1/2}}{2\lambda+1} \\
&\times (ss' - m_{\sigma} m_{\sigma} | \lambda 0)(ss' 00 | \lambda 0) \langle u_s^{\sigma} | \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} | u_{s'}^{\sigma} \rangle,
\end{aligned} \quad (33)$$

where

$$\begin{aligned}
\langle u_s^{\sigma} | \frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} | u_{s'}^{\sigma} \rangle &= \frac{1}{r_{>}^{\lambda+1}} \int_0^r dr' u_s^{\sigma}(r') u_{s'}^{\sigma}(r') r'^{\lambda} \\
&+ r^{\lambda} \int_r^{\infty} dr' u_s^{\sigma}(r') u_{s'}^{\sigma}(r') r'^{-\lambda-1},
\end{aligned} \quad (34)$$

and

$$\left(\frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \right)_A = \frac{A^{\lambda}}{r^{\lambda+1}} \quad \text{if } A < r, \quad (35a)$$

$$\left(\frac{r_{<}^{\lambda}}{r_{>}^{\lambda+1}} \right)_A = \frac{r^{\lambda}}{A^{\lambda+1}} \quad \text{if } A > r. \quad (35b)$$

In these formulas the body-fixed frame is chosen such that the nuclear coordinates are $(0, 0, \pm A)$. The quantity $(ss' - m_{\sigma} m_{\sigma} | \lambda 0)$ is a Clebsch-Gordan coefficient; N_{σ} is the number of electrons in shell σ . Using Eq. (32) and the properties of spherical harmonics we obtain an expression for partial-wave Born matrix elements of the static potential:

$$\langle k'l'm | U^{(s)} | klm \rangle = 2 \left(\frac{2l'+1}{2l+1} \right)^{1/2} \sum_{\lambda=0}^{\infty} (l'\lambda 00 | l0)(l'\lambda m0 | lm) \frac{1}{kk'} \int_0^{\infty} dr n_r(k'r) V_{\lambda}(r) n_l(kr), \quad (36)$$

where $n_l(kr)$ is a Ricatti-Bessel function. As shown by Burke and Sinfallam,⁹ the corresponding exchange matrix element has an expansion of the form

$$\langle k'l'm | U^{(ex)} | klm \rangle = 2 \sum_{\sigma=1}^N \sum_{s,s'\lambda=0}^{\infty} A^{\sigma}(l',l,m,s,s',\lambda) \times R^{\lambda}(n_r, u_s^{\sigma}; u_{s'}^{\sigma}, n_l), \quad (37)$$

where

$$R^{\lambda}(n_r, u_s^{\sigma}; u_{s'}^{\sigma}, n_l) = \frac{1}{kk'} \int_0^{\infty} dr n_r(k'r) u_s^{\sigma}(r) \times \left(\frac{1}{r^{\lambda+1}} \int_0^r dr' u_{s'}^{\sigma}(r') n_l(kr') r'^{\lambda} \right) + r^{\lambda+1} \int_r^{\infty} dr' u_{s'}^{\sigma}(r') n_l(kr') r'^{-\lambda-1}. \quad (38)$$

For a $\sigma(m=0)$ orbital:

$$A^{\sigma}(l',l,m,s,s',\lambda) = \left(\frac{(2s+1)(2s'+1)}{(2l'+1)(2l+1)} \right)^{1/2} (s\lambda 00 | l0) \times (s'\lambda 00 | l'0)(s\lambda 0m | lm) \times (s'\lambda 0m | l'm). \quad (39)$$

The radial function u_{lm}^{σ} in the single-center expansion of the target orbital may be expressed in the form

$$u_{lm}^{\sigma}(r) = r \sum_i C_{\sigma i} \langle Y_{lm}(\hat{\mathbf{r}}) | \mu_i(\hat{\mathbf{r}}) \rangle, \quad (40)$$

where $\mu_i(\hat{\mathbf{r}})$ denotes a Cartesian Gaussian basis function:

$$\mu_i(\hat{\mathbf{r}}) \equiv \mu_{pq\mathbf{s}}^{\alpha\hat{\mathbf{A}}}(\hat{\mathbf{r}}) = N_{pq\mathbf{s}} (x-A_x)^p (y-A_y)^q (z-A_z)^s e^{-\alpha|\hat{\mathbf{r}}-\hat{\mathbf{A}}|^2}, \quad (41)$$

and the coefficients $C_{\sigma i}$ are determined by a self-consistent-field (SCF) calculation. In Eq. (41) $N_{pq\mathbf{s}}$ is a normalization coefficient. Expressions for the radial functions $\langle Y_{lm}(\hat{\mathbf{r}}) | \mu_{pq\mathbf{s}}^{\alpha\hat{\mathbf{A}}}(\hat{\mathbf{r}}) \rangle$ are obtained using the expansion

$$e^{-\alpha|\hat{\mathbf{r}}-\hat{\mathbf{A}}|^2} = 4\pi \sum_{lm} e^{-\alpha(r^2+A^2)} i_l(2\alpha A r) Y_{lm}^*(\hat{\mathbf{A}}) Y_{lm}(\hat{\mathbf{r}}), \quad (42)$$

where $i_l(2\alpha A r)$ is a modified spherical Bessel function. For an s -type Gaussian we find

$$\langle Y_{lm}(\hat{\mathbf{r}}) | \mu_{000}^{\alpha\hat{\mathbf{A}}}(\hat{\mathbf{r}}) \rangle = N_{000} 4\pi e^{-\alpha(r^2+A^2)} i_l(2\alpha A r) Y_{lm}^*(\hat{\mathbf{A}}), \quad (43)$$

and for a p_z type:

$$\langle Y_{lm}(\hat{\mathbf{r}}) | \mu_{001}^{\alpha\hat{\mathbf{A}}}(\hat{\mathbf{r}}) \rangle = N_{001} 4\pi e^{-\alpha(r^2+A^2)} \left[\left(\frac{(l+m+1)(l-m+1)}{(2l+1)(2l+3)} \right)^{1/2} r i_{l+1}(2\alpha A r) Y_{l+1,m}^*(\hat{\mathbf{A}}) + \left(\frac{(l+m)(l-m)}{(2l+1)(2l-1)} \right)^{1/2} r i_{l-1}(2\alpha A r) Y_{l-1,m}^*(\hat{\mathbf{A}}) - A_z i_l(2\alpha A r) Y_{lm}^*(\hat{\mathbf{A}}) \right] \quad (44)$$

where A_z is the z component of $\hat{\mathbf{A}}$.

III. CALCULATIONS AND RESULTS

The truncated static-exchange potential U^t is calculated in two steps as described in Ref. 1. The first step involves a SCF calculation for the occupied target orbitals. We use a standard basis set of contracted Cartesian Gaussian functions, referred to as the target basis. In the second-step matrix elements of the static-exchange potential, defined by Eq. (27), are computed over a set of uncontracted functions, i.e., the scattering basis. For a closed-shell, homonuclear diatomic, the K matrix is block diagonal in the symmetries $^2\Sigma_g$,

$^2\Sigma_u$, $^2\Pi_u$, $^2\Pi_g$, In this work we consider scattering in the Σ and Π channels. To investigate the convergence of the scattering basis, we have chosen several basis sets for each symmetry. The basis set calculations are carried out using standard molecular-bound-state programs.

In the SCF calculation for the σ_g occupied orbital, we used a $(10s5p_z)$ set of primitive Gaussians contracted to $[7s5p_z]$ on each nucleus. The exponents and contraction coefficients for this basis are those of Huzinaga¹⁰ and are listed in Table I(a). The quadrupole moment of H_2 in this basis is 0.478 a.u. In our investigation of scattering basis

TABLE I. Basis sets.

Type ^a	Center ^b	Exponent	Contraction coefficient ^c
(a) Valence Σ basis set			
1. (000)	(0,0, ± 0.7003)	1685.517	0.004 227 3
2. (000)	(0,0, ± 0.7003)	249.958 4	0.035 026
3. (000)	(0,0, ± 0.7003)	55.658 34	0.192 038 9
4. (000)	(0,0, ± 0.7003)	15.274 3	0.833 376 4
5. (000)	(0,0, ± 0.7003)	4.862 8	
6. (000)	(0,0, ± 0.7003)	1.731 6	
7. (000)	(0,0, ± 0.7003)	0.668 05	
8. (000)	(0,0, ± 0.7003)	0.274 37	
9. (000)	(0,0, ± 0.7003)	0.116 98	
10. (000)	(0,0, ± 0.7003)	0.041 133	
11. (001)	(0,0, ± 0.7003)	4.8	
12. (001)	(0,0, ± 0.7003)	2.53	
13. (001)	(0,0, ± 0.7003)	1.33	
14. (001)	(0,0, ± 0.7003)	0.701	
15. (001)	(0,0, ± 0.7003)	0.369	
(b) Σ_g symmetry basis set of diffuse single-center Gaussians			
1. (000)	(0,0,0)	1.0	
2. (000)	(0,0,0)	0.5	
3. (000)	(0,0,0)	0.25	
4. (000)	(0,0,0)	0.15	
5. (000)	(0,0,0)	0.09	
6. (000)	(0,0,0)	0.054	
7. (000)	(0,0,0)	0.03	
8. (000)	(0,0,0)	0.02	
9. (000)	(0,0,0)	0.01	
10. (000)	(0,0,0)	0.005	
11. (000)	(0,0,0)	0.002	
12. (000)	(0,0,0)	0.0006	
(c) Σ symmetry basis set of diffuse two-center Gaussians			
1. (000)	(0,0, ± 0.7003)	0.027	
2. (000)	(0,0, ± 0.7003)	0.016 9	
3. (000)	(0,0, ± 0.7003)	0.010 6	
4. (000)	(0,0, ± 0.7003)	0.006 63	
5. (000)	(0,0, ± 0.7003)	0.004 14	
6. (000)	(0,0, ± 0.7003)	0.002 58	
7. (000)	(0,0, ± 0.7003)	0.001 61	
8. (000)	(0,0, ± 0.7003)	0.001 01	
9. (000)	(0,0, ± 0.7003)	0.000 631	
10. (000)	(0,0, ± 0.7003)	0.000 394	
11. (001)	(0,0, ± 0.7003)	0.194	
12. (001)	(0,0, ± 0.7003)	0.102	
(d) Π_x symmetry basis set			
1. (100)	(0,0, ± 0.7003)	15.274 3	
2. (100)	(0,0, ± 0.7003)	4.862 8	
3. (100)	(0,0, ± 0.7003)	1.731 6	
4. (100)	(0,0, ± 0.7003)	0.668 05	
5. (100)	(0,0, ± 0.7003)	0.274 37	
6. (100)	(0,0, ± 0.7003)	0.116 98	
7. (100)	(0,0, ± 0.7003)	0.041 133	
8. (100)	(0,0, ± 0.7003)	0.027 0	
9. (100)	(0,0, ± 0.7003)	0.016 9	
10. (100)	(0,0, ± 0.7003)	0.010 6	
11. (100)	(0,0, ± 0.7003)	0.006 63	
12. (100)	(0,0, ± 0.7003)	0.004 14	
13. (100)	(0,0, ± 0.7003)	0.002 58	
14. (100)	(0,0, ± 0.7003)	0.001 61	
15. (100)	(0,0, ± 0.7003)	0.001 01	

^a (pqs) in Eq. (40).^b Coordinates of basis function center(s).^c Contraction coefficients refer to SCF target basis set only.

sets, we have primarily studied the Σ symmetries since these dominate the scattering cross section at low energy. One of the Σ basis sets Table I(a), consists of the same (10s5pz) sets of primitives used in the SCF calculation. Two other basis sets were formed by augmenting this basis with diffuse functions placed either at the center of mass or at the nuclei. One of these basis sets consists of sets (a) and (b) in Table I, the other consists of sets (a) and (c). A fourth basis set consisting only of the (10s) part of the SCF primitive basis (functions 1–10 in set (a), Table I) was also tested. For Π channel scattering we chose basis sets consisting of seven and fifteen p_x -type Gaussians centered at the nuclei (functions 1–7 and 1–15 in set (d), Table I). Our techniques for calculating the matrix elements $\langle klm | K^t | k'l'm \rangle$ and $\langle klm | U^t | k'l'm \rangle$ using Eqs. (15) and (23) are described in Ref. 1.

In the calculation of exact partial-wave Born matrix elements of the static-exchange potential, we included six partial waves ($l=0, 2, \dots, 10$) in the single-center expansion of the $H_2\sigma_g$ orbital. This expansion is sufficient to converge the quadrupole moment to within two parts in 10^6 of the exact value for our choice of target basis. The radial integrals occurring in the multipole expansion of the static potential, and in the direct and exchange potential partial-wave Born matrix elements, are computed using Simpson's rule quadrature. Most of the computational effort in this procedure involves the exchange Born matrix elements since these require a two-dimensional numerical quadrature. Fortunately, the partial-wave expansions occurring in these matrix elements are quite rapidly convergent. The cutoffs for these partial wave sums were chosen to converge the exchange matrix elements to one part in 10^5 .

The third and fourth terms in our variational correction formula, Eq. (25), involve a principal value integration with respect to k'' . These integrals are evaluated using a Simpson's-rule quadrature except in a small region around the singularity. In this region the coefficient of $(k - k'')^{-1}$ in the integrand is approximated by a Taylor series expansion and the integral is treated analytically. The sum over l'' in these terms converges rapidly for low scattering energy. In this work we included l'' up to five and obtained convergence to three significant figures.

Variationally corrected K matrix elements are shown in Table II for the basis sets described above. Table II also shows the corresponding uncorrected matrix elements. The effectiveness of our correction formula is indicated by the consistency of the variationally corrected K matrix results for different basis sets. In contrast there

TABLE II. Variationally corrected K -matrix elements.

$m\ l\ l'$	Basis	$k = 0.5$				$k = 0.7$			
		$K_{ll'm}^t$	$K_{ll'm}^s$	Born correction ^a	Non-Born correction ^b	$K_{ll'm}^t$	$K_{ll'm}^s$	Born correction	Non-Born correction
0 0 0	A^c	-1.529	-1.545	4.39(-2)	2.78(-2)	-3.241	-3.327	-2.93(-3)	-8.29(-2)
	B^d	-1.472	-1.498	-3.5(-3)	-2.16(-2)	-3.576	-3.596	-7.31(-4)	-2.00(-2)
	C^e	-1.540	-1.512	-2.11(-2)	7.2(-3)	-3.531	-3.646	-1.57(-2)	-9.79(-2)
	D^f	-1.563	-1.552	-6.06(-2)	7.16(-2)	-3.459	-3.588	-4.94(-3)	-1.24(-1)
0 2	A	-0.29(-2)	1.44(-2)	-1.6(-3)	1.89(-2)	-8.02(-3)	6.06(-3)	-9.67(-3)	2.38(-2)
	B	1.74(-2)	1.46(-2)	-2.9(-3)	1.1(-4)	8.57(-3)	5.08(-3)	-3.06(-3)	-4.21(-4)
	C	2.32(-2)	1.36(-2)	-2.9(-3)	-7.31(-3)	9.59(-3)	6.77(-3)	3.07(-3)	-5.89(-3)
	D	-2.89(-2)	1.15(-2)	-7.52(-3)	4.79(-2)	-1.27(-1)	-1.41(-2)	-2.79(-2)	1.41(-1)
2 2	A	1.98(-2)	1.71(-2)	-5.0(-4)	-2.22(-3)	6.68(-2)	3.61(-2)	-2.27(-2)	-7.94(-3)
	B	1.87(-2)	1.74(-2)	-1.3(-3)	-2.0(-5)	6.47(-2)	3.74(-2)	-2.39(-2)	-3.36(-3)
	C	6.02(-2)	1.54(-2)	-3.98(-2)	-5.02(-3)	4.64(-2)	3.83(-2)	-8.38(-3)	2.66(-4)
	D	-0.05(-2)	1.78(-2)	1.66(-2)	1.75(-3)	-4.65(-3)	3.97(-2)	3.39(-2)	1.05(-2)
1 1	A	4.46(-1)	4.27(-1)	-4.1(-3)	-1.52(-2)	8.78(-1)	8.64(-1)	-3.93(-2)	2.48(-2)
	C	4.68(-1)	4.40(-1)	-1.08(-3)	-1.73(-2)	9.09(-1)	8.70(-1)	-3.57(-2)	-3.07(-3)
	D	4.49(-1)	4.27(-1)	-3.52(-3)	-1.81(-2)	8.83(-1)	8.52(-1)	-4.18(-2)	9.98(-3)
1 3	A	5.73(-3)	7.46(-3)	3.58(-3)	-1.86(-3)	2.08(-2)	1.49(-2)	1.76(-3)	-7.64(-3)
	C	1.70(-2)	7.08(-3)	-8.53(-3)	1.38(-3)	2.69(-2)	1.50(-2)	5.79(-3)	-6.08(-3)
	D	2.41(-3)	7.31(-3)	5.42(-3)	-5.20(-4)	9.37(-3)	1.35(-2)	7.19(-3)	-3.04(-3)
3 3	A	1.50(-3)	5.52(-3)	4.20(-3)	-1.75(-4)	1.03(-2)	8.81(-3)	1.00(-4)	-1.38(-3)
	C	1.13(-2)	5.08(-3)	-5.08(-3)	-1.10(-3)	2.39(-2)	8.32(-3)	-1.33(-2)	-2.25(-3)
	D	1.3(-5)	5.58(-3)	5.57(-3)	-5.1(-6)	9.9(-5)	9.24(-3)	9.20(-3)	-6.6(-5)
1 1 1	E^g	1.15(-1)	1.08(-1)	-5.06(-3)	-2.46(-3)	2.41(-1)	2.19(-1)	-2.41(-2)	1.99(-3)
	F^h	1.15(-1)	1.08(-1)	-5.69(-3)	-1.12(-3)	2.36(-1)	2.19(-1)	-1.61(-2)	-3.37(-4)
2 2	E	1.43(-2)	1.11(-2)	-3.13(-3)	-6.0(-5)	4.66(-2)	2.70(-2)	-1.71(-2)	-2.39(-3)
	F	1.11(-2)	1.12(-2)	8.4(-5)	5.5(-6)	3.76(-2)	2.76(-2)	-8.86(-3)	-1.10(-3)

^a Second term on RHS of Eq. (25).^b Terms three and four on RHS of Eq. (25).^c Basis set (a) in Table I.^d Basis sets (a) and (b) in Table I.^e Basis sets (a) and (c) in Table I.^f Basis functions 1-10 in set (a), Table I.^g Basis functions 1-7 in set (d), Table I.^h Basis set (d), Table I.

is considerable variation in the uncorrected results for nondiagonal and higher partial-wave matrix elements. Table II shows the total variational correction divided into the Born part (the second term on the RHS of Eq. (25)) and the non-Born part (the sum of terms three and four). These results show that in general neither the Born nor the non-Born term dominates the total correction.

Table III compares our variationally corrected diagonal phase shifts, $\delta_{lm} = \tan^{-1} K_{llm}$, with the static-exchange results of Schneider⁶ and Tully and Berry.⁷ The results shown are for the (10s5p_z) Σ basis set (set (a), Table I) and the (7p_x) Π_x basis set (functions 1-7 in set (d), Table I). The error estimates in Table III correspond to the observed differences in the corrected results for different basis sets. The size of these differences is generally greater than the numerical uncertainty of our calculation. Part of this error is due to our

neglect of the last term on the RHS of Eq. (21). As Table III shows, the agreement between our results and the other calculated results is very good. The largest discrepancy occurs for the $d\sigma$ phase shift ($l=2, m=0$) for which our result is 50% larger than the other calculated values. This discrepancy may be due to the use of slightly different target wave functions in the three calculations. Table III also shows our results for first and second Born-approximation phase shifts. These results show that the first Born approximation is valid for d -wave phase shifts at 3.40 and 6.67 eV scattering energies. The second Born approximation is accurate for the $p\pi$ phase shift and gives significantly better results for the $p\sigma$ phase shift than the first Born approximation. Both levels of Born approximation give poor results for the s -wave phase shifts. The accuracy of the corrected $d\sigma$ phase shift is verified by the Born results.

TABLE III. Diagonal phase-shift results.

$l \ m \ k$	Corrected phase shift ^a	Reference 6	Reference 7	Born ^b	Second Born ^c
0 0 0.5	2.14 \pm 0.02 ^d	2.122	2.174	1.256	1.503
0 0 0.7	1.86 \pm 0.02	1.797		1.249	1.445
1 0 0.5	0.40 \pm 0.02	0.3891	0.368	0.178	0.323
1 0 0.7	0.71 \pm 0.02	0.7005	0.688	0.310	0.558
2 0 0.5	0.017 \pm 0.002	0.0101	0.012	0.018	0.0181
2 0 0.7	0.036 \pm 0.002	0.0333		0.038	0.0384
1 1 0.5	0.108 \pm 0.002	0.1043	0.108	0.076	0.1184
1 1 0.7	0.215 \pm 0.002	0.2138	0.216	0.156	0.2368
2 1 0.5	0.011 \pm 0.002	0.0108	0.009	0.011	0.0117
2 1 0.7	0.027 \pm 0.002	0.0278		0.026	0.0297

^a $\delta_{lm} = \tan^{-1} K_{lm}^s$, Σ phase-shift basis is set (a), Table I; Π phase-shift basis is set (d), Table I, functions 1-7.

^bBorn approximation.

^cSecond Born approximation, defined by Eq. (26).

^dError estimates reflect the variation of corrected results for different basis sets.

IV. DISCUSSION AND CONCLUSIONS

The results show that our method for computing a variational correction to the elastic scattering K matrix significantly improves the accuracy of our basis set results. The accuracy of the method applied to e^- -H₂ scattering in the static-exchange approximation is confirmed by (a) comparison with the results of Schneider⁶ and Tully and Berry,⁷ (b) the stability of our corrected results against changes in the trial basis set, and (c) comparison with first and second Born-approximation results for higher partial-wave matrix elements.

An advantage of the present method of obtaining variationally stable scattering results is that it may be applied at any scattering energy. In a previous paper,¹ we argued that our uncorrected basis-sets results are approximately variationally stable at eigenenergies of the basis-set representation of the Hamiltonian. The argument for variational stability at eigenenergies is valid only at low-scattering energy since it depends on an approximation of the boundary conditions for a non-spherical potential. The difficulty of treating non-

spherical potential-boundary conditions appears to be inherent in all eigenvalue methods for variational stability developed for spherical potentials.

Table II shows that higher partial-wave K matrix elements and nondiagonal matrix elements are most improved by the variational correction. These matrix elements are small in the present case, but are probably larger for most other systems of interest. Hence, we expect the variational correction will be important in basis-set calculations for scattering from larger targets. The calculation of variationally corrected K matrix elements for e^- -N₂ and e^- -CO₂ scattering in the static-exchange approximation is in progress.

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